Electronic Supplementary Material (ESI) for Chemical Science.

Supporting Information

Tailoring Lewis/Brønsted acid properties of MOF nodes via hydrothermal and solvothermal synthesis: simple approach with exceptional catalytic implications

Sergio Rojas-Buzo,[a] Benjamin Bohigues,[a] Christian W. Lopes,[b] Débora M. Meira,[c,d] Mercedes Boronat,[a] Manuel Moliner*[a] and Avelino Corma*[a]

[a]Instituto de Tecnología Química, Universitat Politècnica de València - Consejo Superior de Investigaciones Científicas, Av. de los Naranjos, s/n, 46022 Valencia, Spain

[b]Institute of Chemistry, Universidade Federal do Rio Grande do Sul – UFRGS, Av. Bento Gonçalves, 9500, 91501-970 Porto Alegre, RS, Brazil.

[c]CLS@APS, Advanced Photon Source, Argonne National Laboratory, 9700 S. Cass Avenue, Argonne, IL 60439, USA.

[d]Canadian Light Source Inc., 44 Innovation Boulevard, Saskatoon, Saskatchewan S7N 2V3, Canada.

*Corresponding authors: mmoliner@itq.upv.es, acorma@itq.upv.es

Figure S1. Hf-MOF-808 models used in the DFT simulations. The transferred proton in structures B and D, and the additional water molecules in E, F, G and H are marked with a blue circle. C and O atoms are depicted as gray and red sticks, Hf and H as cyan and white balls. The additional water molecules in G and H are not accessible for interaction with TMPO.

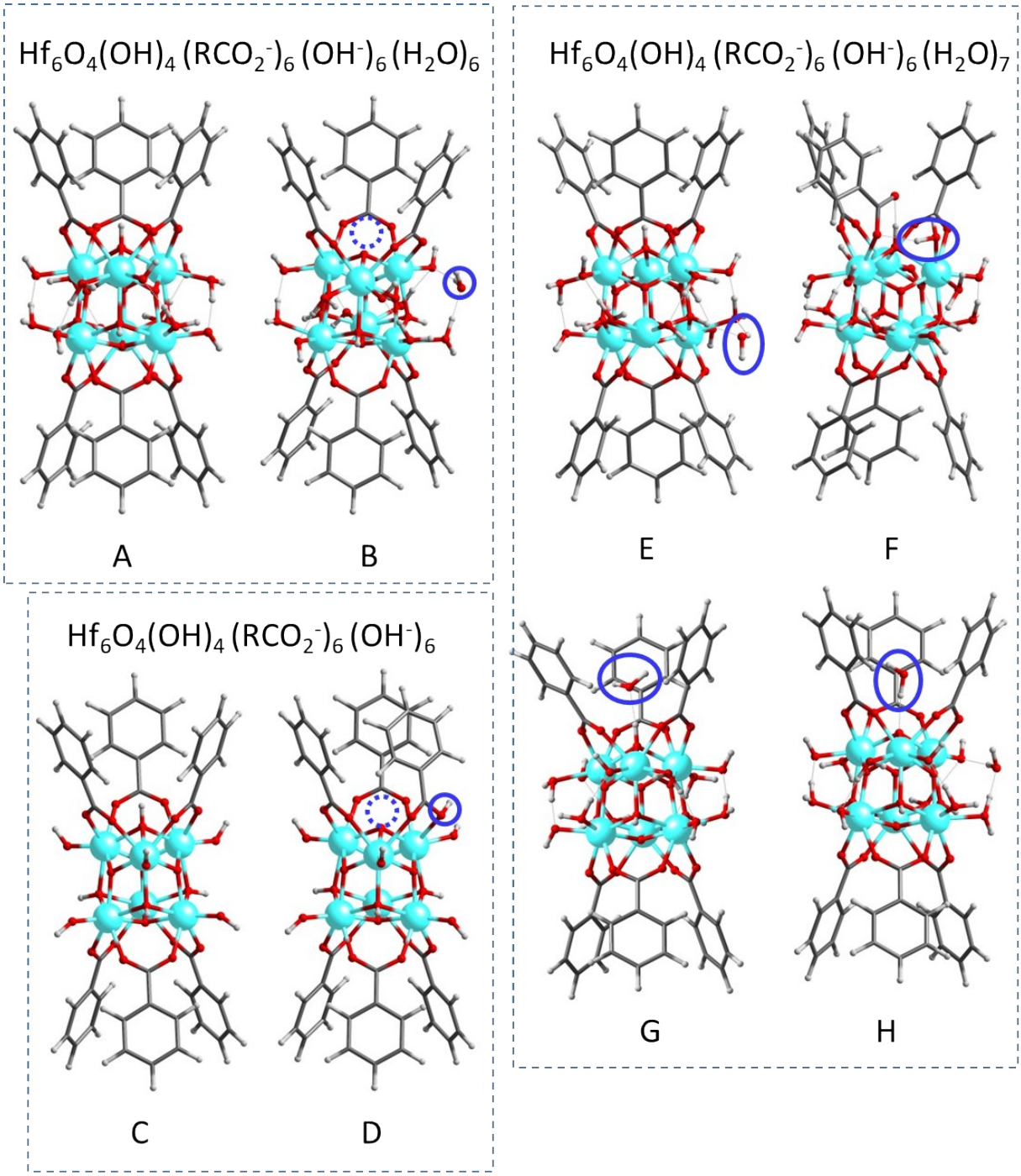


Figure S2. N_2 adsorption and desorption isotherms of Hf-MOF-808_H_2O (red triangles) and Hf-MOF-808_DMF (blue circles) materials.

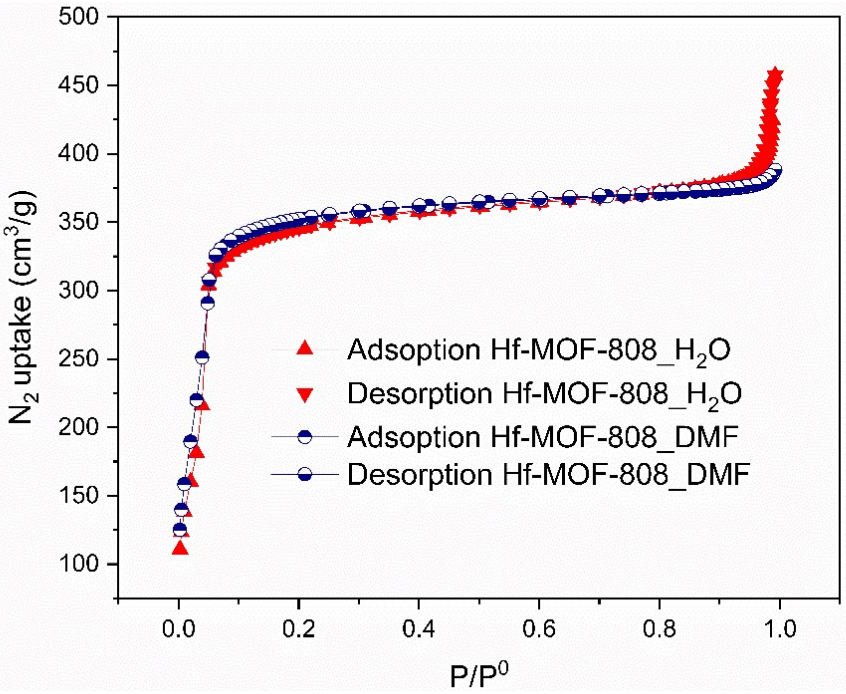


Figure S3. FTIR spectra of Hf-MOF-808_H_2O (red line) and Hf-MOF-808_DMF (blue line) together with the FTIR spectrum of the organic ligand (black line) employed in its preparation.

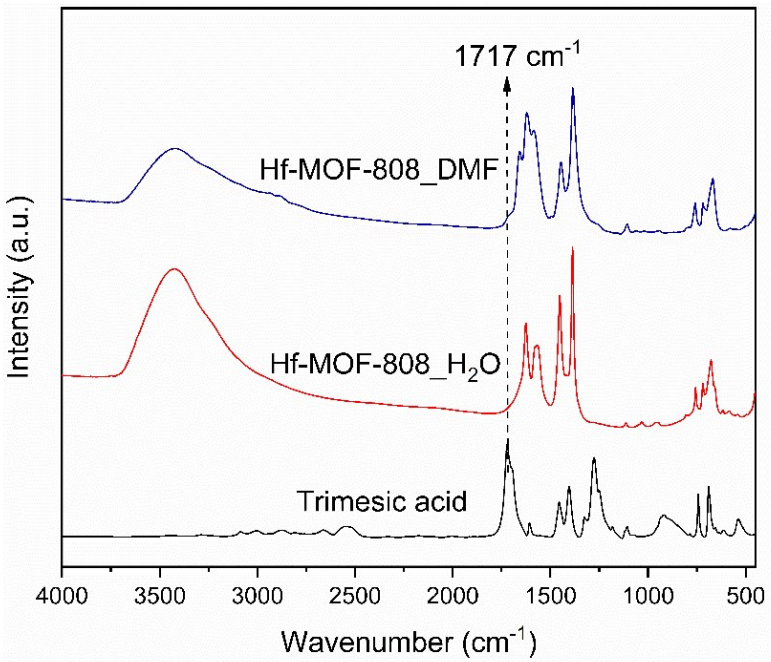


Figure S4. Thermogravimetric analysis of Hf-MOF-808_H_2O (red line) and Hf-MOF-808_DMF (blue line).

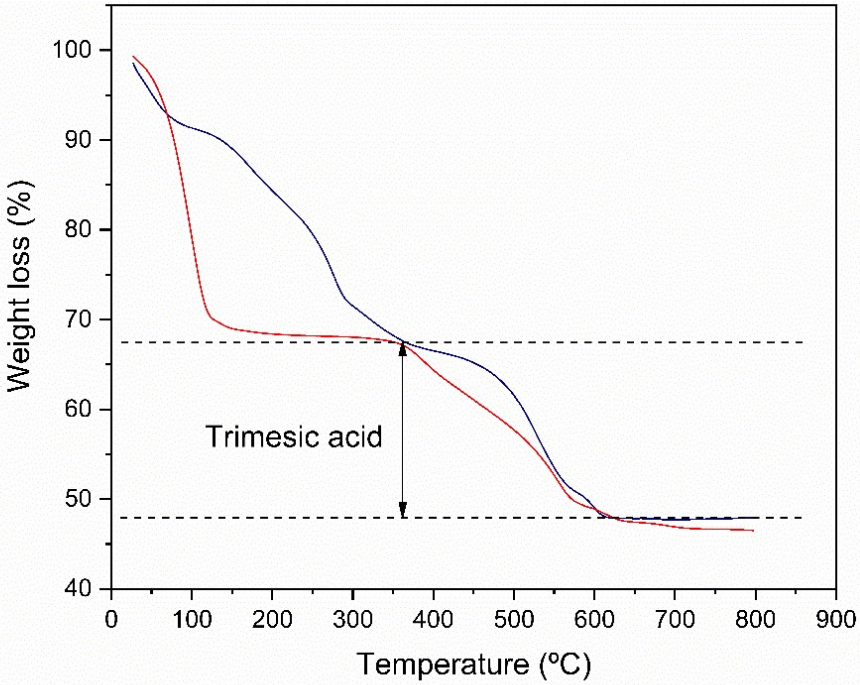


Figure S5. Curve fitting for the Hf4f XPS spectra of Hf-MOF-808_DMF (bottom) and Hf-MOF-808_H_2O (top).

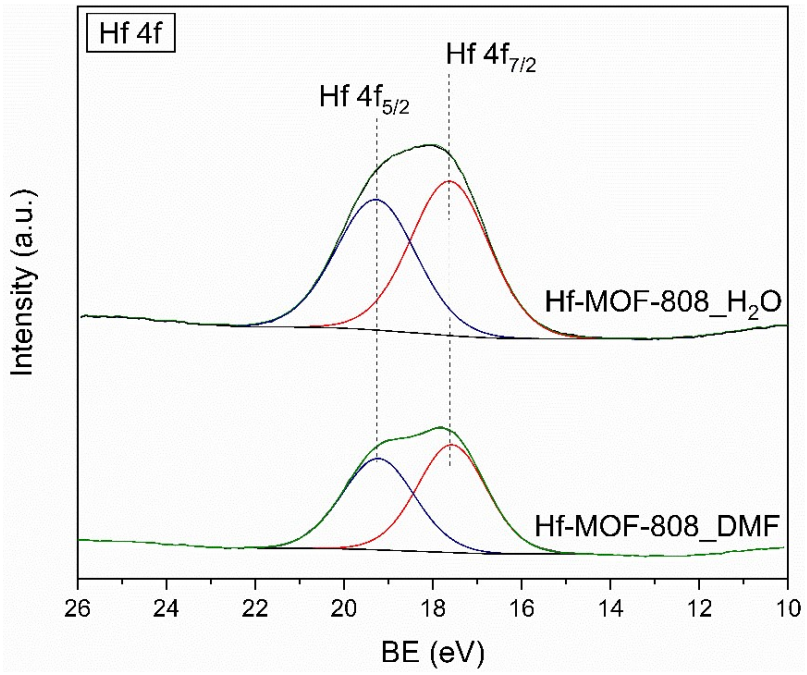


Figure S6. Curve-fittings and |FT| of the k^3-weighted χ(k) functions of Hf-MOF-808_H_2O (red) and Hf-MOF-808_DMF (blue).

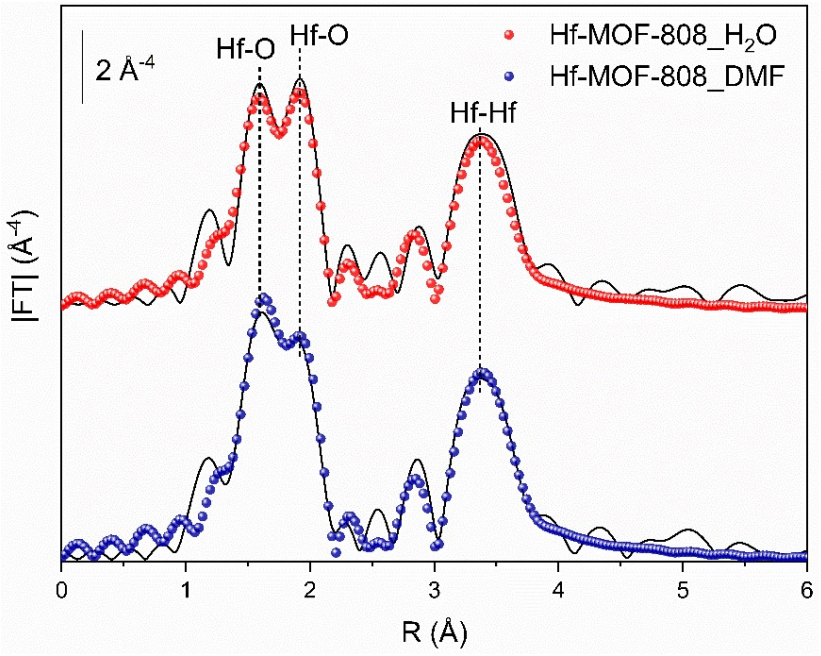


Figure S7. Kinetic profiles for α-pinene oxide conversion employing Hf-MOF-808_H_2O (red circles) and Hf-MOF-808_DMF (blue squares) as catalysts.

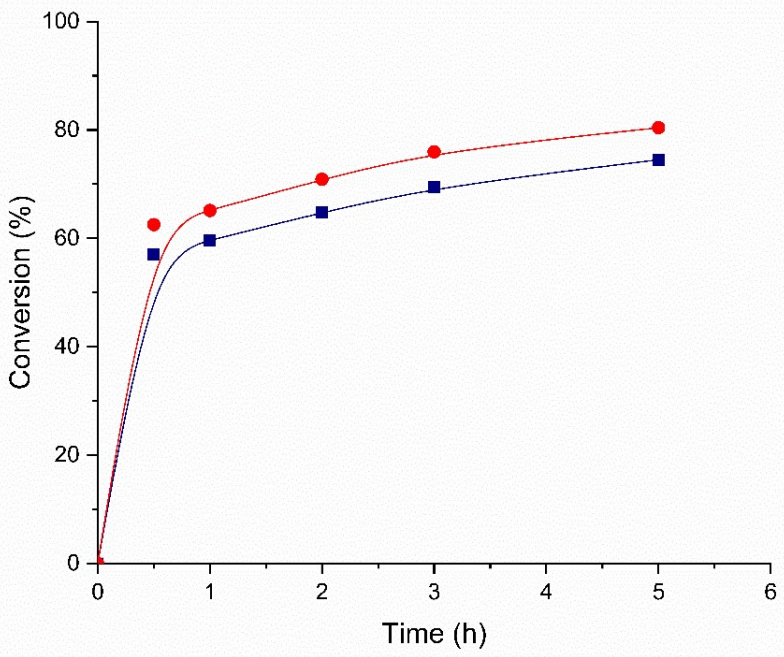


Figure S8. Product selectivity for the isomerization of α-pinene oxide at 75-80% conversion employing Hf-MOF-808_H_2O and Hf-MOF-808_DMF as catalysts. The dotted line indicates the selectivity of 55%.

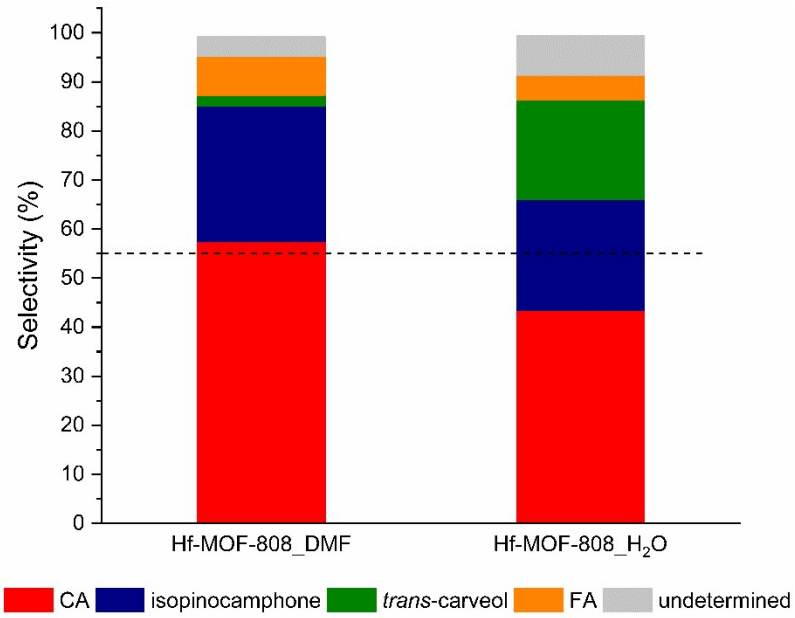
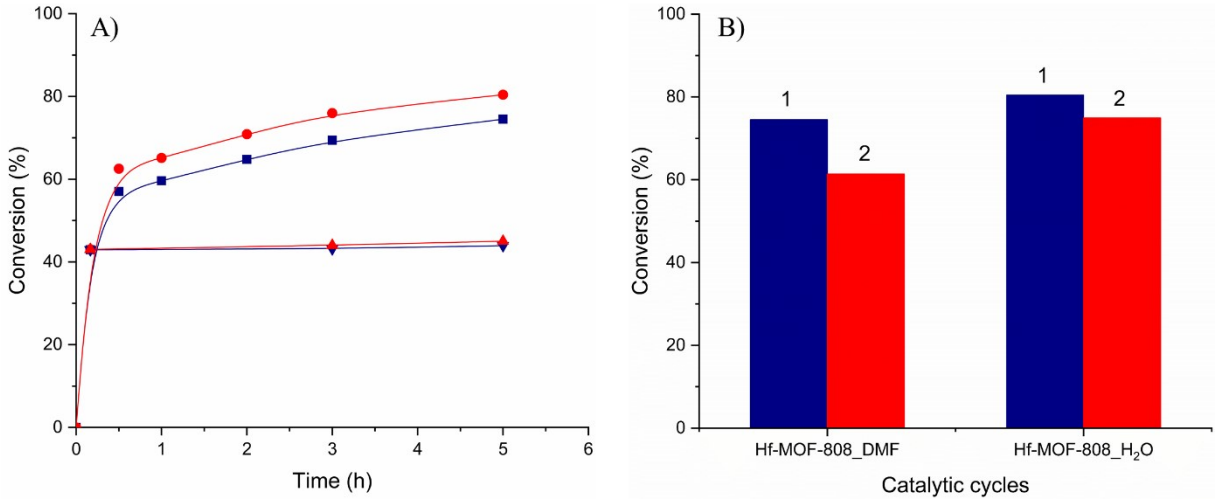


Figure S9. A) Hot filtration test of Hf-MOF-808_H_2O (red triangles) and Hf-MOF-808_DMF (blue triangles). B) Recyclability test of Hf-MOF-808_H_2O and Hf-MOF-808_DMF after two consecutive runs for the isomerization of α-pinene oxide.



Scheme S1. α-pinene oxide isomerization catalyzed by Hf-MOF-808.

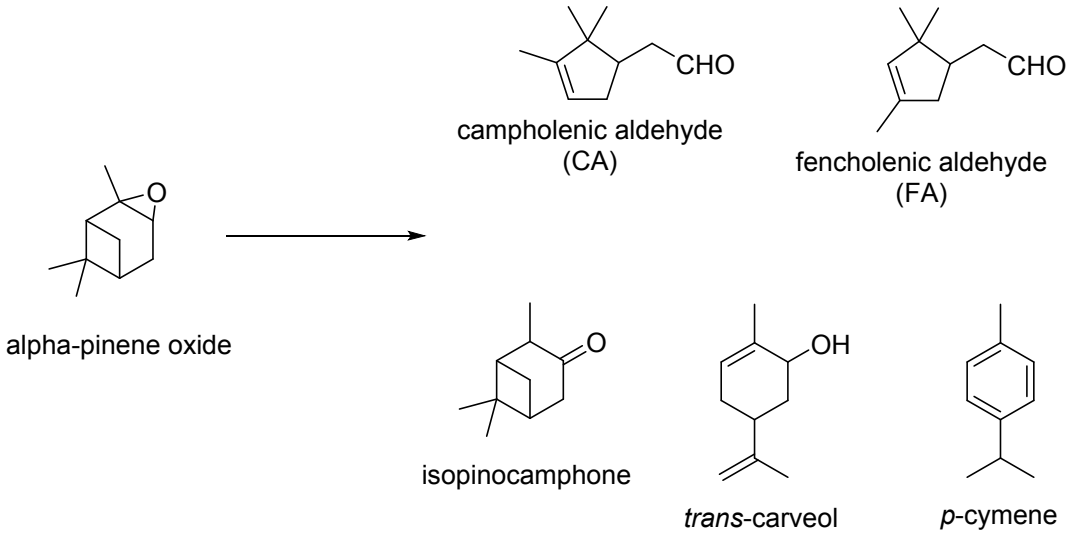


Table S1. Relative amount of Brønsted and Lewis acid sites obtained from ^{31}P MAS NMR spectra when TMPO was adsorbed onto Hf-MOF-808_H_2O (P/Hf molar ratio=0.18) and Hf-MOF-808_DMF (P/Hf molar ratio=0.21). Integrated ^{31}P peak area normalized at X ppm are calculated as: (mol P/g-cat)(mol Hf/g-cat)$^{-1}$(area % at δ=X ppm). TOF values were calculated for the epoxide ring-opening (ERO) and Meerwein-Ponndorf-Verley (MPV) reactions.

Sample	Acid site	δ ^{31}P (ppm)	Integrated ^{31}P area (a.u.)	% area	Integrated area normalized (%)	Ratio Brønsted/Lewis acid sites	Ratio ERO/MPV TOFs
Hf-MOF-808_H_2O	Lewis	55	14340	4.17	0.75	2.41	4.41
		58	86555	25.16	4.53		
	Brønsted	62	202195	58.77	10.59		
		68	40958	11.90	2.14		
Hf-MOF-808_DMF	Lewis	56	203220	57.90	12.16	0.26	0.42
		58	74419	21.20	4.45		
	Brønsted	62	59814	17.04	3.58		
		69	13512	3.85	0.81		

Table S2. Isotropic δ(^{31}P) chemical shifts and optimized PO bond lengths calculated for TMPO interacting with different sites in Hf-MOF-808 catalyst models.

Model	Site	δ(^{31}P) (ppm)	r(PO) (Å)
A	Hf	52	1.521
A	μ3-OH	48	1.521
B	H^+	68	1.554
C	Hf	52	1.520
C	μ3-OH	48	1.519
D	H^+	86	1.578
E	H_2O	42	1.514
F	H_2O	43	1.516

Table S3. Summary of optimized parameters by fitting the Hf L_3-edge EXAFS data.[a]

Parameter	Hf-MOF-808_H_2O	Hf-MOF-808_DMF
$N_{Hf\text{-}O1}$	2.4 ± 0.5	3.0 ± 0.4
$R_{Hf\text{-}O1}$ (Å)	2.060 ± 0.018	2.085 ± 0.013
$N_{Hf\text{-}O2}$	3.7 ± 0.7	3.9 ± 0.6
$R_{Hf\text{-}O2}$ (Å)	2.225 ± 0.015	2.242 ± 0.013
$\sigma^2_{Hf\text{-}O}$ (Å^2)	0.0036 ± 0.0012	
$N_{Hf\text{-}Hf}$	3.4 ± 1.1	3.8 ± 1.2
$R_{Hf\text{-}Hf}$ (Å)	3.498 ± 0.009	3.506 ± 0.005
$\sigma^2_{Hf\text{-}Hf}$ (Å^2)	0.0043 ± 0.0011	
ΔE_0 (eV)	7.2 ± 0.9	
r-factor (%)	0.049	0.034

[a]The fits were performed up to the second coordination shell over FT of the k^3-weighted χ(k) functions performed in the Δk = 2.0-13.3 Å^{-1} and ΔR = 1.1-4.0 Å intervals, resulting into a number of independent parameters of 41. S_0^2 = 1.0.